

**LYCEN 9145**  
November 1991

## **SYMMETRY ADAPTATION IN TWO-PHOTON SPECTROSCOPY**

Maurice Kibler

Institut de Physique Nucléaire de Lyon  
IN2P3-CNRS et Université Claude Bernard  
43 Boulevard du 11 Novembre 1918  
F-69622 Villeurbanne Cedex, France

### **ABSTRACT**

Symmetry adaptation techniques are applied to the determination of the intensity of two-photon transitions for transition ions in finite symmetry environments. We treat the case of intra-configurational transitions with some details and briefly report some results on inter-configurational transitions. In particular, for intra-configurational transitions, we describe a model which takes into account the following ingredients : (symmetry, second- plus third-order mechanisms,  $S$ -,  $L$ - and  $J$ -mixings).

Invited lecture at the "Second International School on Excited States of Transition Elements", Wrocław-Karpacz, Poland, 2 - 6 September 1991. Published in **Excited States of Transition Elements**, Eds. **W. Stręk, W. Ryba-Romanowski, J. Legendziewicz, and B. Jezowska-Trzebiatowska** (World Scientific, Singapore, 1992), p. 139-148.

# SYMMETRY ADAPTATION IN TWO-PHOTON SPECTROSCOPY

Maurice Kibler

Institut de Physique Nucléaire de Lyon  
IN2P3-CNRS et Université Claude Bernard  
F-69622 Villeurbanne Cedex, France

## ABSTRACT

Symmetry adaptation techniques are applied to the determination of the intensity of two-photon (intra- and inter-configurational) transitions for transition ions in finite symmetry environments.

## 1. INTRODUCTION

Symmetry adaptation techniques, developed in the spirit of Refs. [1,2], for a chain of groups  $O(3) \supset G$  are applied here to two-photon spectroscopy of transition ions of configuration  $n\ell^N$  ( $\ell = d$  for transition metal ions and  $\ell = f$  for lanthanide or actinide ions) in surroundings of finite symmetry  $G$ . More precisely, we show in this lecture how Wigner-Racah calculus for a chain  $O(3) \supset G$  (in terms of simple or double groups) can be combined with models<sup>3–20</sup> based on second- plus third-order mechanisms in order to isolate the polarization dependence from the intensity of two-photon transitions for an  $n\ell^N$  ion in a molecular or solid-state environment with symmetry  $G$ . (For classification and symmetry-breaking purposes, the group  $G$  may be replaced by a chain of subgroups of  $O(3)$ , the relevant symmetry group being one of the groups of the chain.)

The rôle of symmetries in two-photon spectroscopy of partly-filled shell ions in finite symmetry is touched upon in Refs. [4-6,12-14,16,17]. In Refs. [4,5], the information arising from symmetry is handled mainly in a qualitative way. More quantitative results can be found in Refs. [6,12-14,16,17]. In Ref. [12], the accent is put on the transition matrix elements between initial and final state vectors while emphasis is on the intensity strength in Refs. [14,16] and in the present lecture. This lecture constitutes a complement to the material presented in Refs. [14,16].

Two distinct cases are studied in this work. The case of  $(n\ell^N \rightarrow n\ell^N$ , e.g.,  $3d^N \rightarrow 3d^N$  and  $4f^N \rightarrow 4f^N$ ) intra-configurational two-photon transitions, which are parity allowed, is worked out in section 2 and the one of  $(n\ell^N \rightarrow n\ell^{N-1}n'\ell'$  with  $\ell + \ell'$  odd, e.g.,  $3d^N \rightarrow 3d^{N-1}4p$  and  $4f^N \rightarrow 4f^{N-1}5d$ ) inter-configurational two-photon transitions, which are parity forbidden, is examined in section 3.

## 2. INTRA-CONFIGURATIONAL TWO-PHOTON TRANSITIONS

### 2.1. Preliminaries

We know that the electronic transition matrix element  $M_{i \rightarrow f}$  between an initial state  $i$  and a final state  $f$  is, in the framework of the electric dipolar ap-

proximation, given by

$$M_{i \rightarrow f} = \sum_v \frac{1}{\Delta_1} \left( f | \vec{D} \cdot \vec{\mathcal{E}}_2 | v \right) \left( v | \vec{D} \cdot \vec{\mathcal{E}}_1 | i \right) + \sum_v \frac{1}{\Delta_2} \left( f | \vec{D} \cdot \vec{\mathcal{E}}_1 | v \right) \left( v | \vec{D} \cdot \vec{\mathcal{E}}_2 | i \right) \quad (1)$$

The two summations in (1) have to be extended over all the intermediate states  $v$  having a parity different from the one of the states  $i$  and  $f$ . Furthermore, we have  $\Delta_\lambda = \hbar\omega_\lambda - E_v$ , where  $E_v$  is the energy of the state  $v$  with respect to that of the state  $i$  and  $\hbar\omega_\lambda$  the energy of the photon no.  $\lambda$ . (For Raman scattering, the sign of  $\hbar\omega_2$  has to be changed.) The quantity  $\vec{D} \cdot \vec{\mathcal{E}}_\lambda$  in (1) stands for the scalar product of the electric dipolar moment operator  $\vec{D}$  for the  $N$  electrons and the unit polarization vector  $\vec{\mathcal{E}}_\lambda$  for the photon no.  $\lambda$ . (We use single-mode excitations, of energy  $\hbar\omega_\lambda$ , wave-vector  $\vec{k}_\lambda$  and polarization  $\vec{\mathcal{E}}_\lambda$ , for the radiation field.) The two photon beams can be polarized either circularly with

$$(\mathcal{E}_\lambda)_q = -\delta(q, -1) \quad \text{if} \quad \vec{\mathcal{E}}_\lambda = \vec{e}_{+1} \quad \text{while} \quad (\mathcal{E}_\lambda)_q = -\delta(q, +1) \quad \text{if} \quad \vec{\mathcal{E}}_\lambda = \vec{e}_{-1} \quad (2)$$

or linearly with

$$(\mathcal{E}_\lambda)_0 = \cos \theta_\lambda \quad (\mathcal{E}_\lambda)_{\pm 1} = \mp \frac{1}{\sqrt{2}} \sin \theta_\lambda \exp(\pm i\varphi_\lambda) \quad (3)$$

In equations (2) and (3), we use the components  $(\mathcal{E}_\lambda)_q = \vec{\mathcal{E}}_\lambda \cdot \vec{e}_q$  (with  $q = -1, 0, 1$  and  $\lambda = 1, 2$ ) in the standard spherical basis  $(\vec{e}_{-1}, \vec{e}_0, \vec{e}_{+1})$ . In the case of a linear polarization, the angles  $(\theta_\lambda, \varphi_\lambda)$  are the polar angles of the polarization vector  $\vec{\mathcal{E}}_\lambda$  ( $\lambda = 1, 2$ ) with respect to the crystallographic  $c$ -axis. For two-photon absorption, only one sum occurs in (1) when the two photons are identical.

Equation (1) can be derived from the time-dependent perturbation theory and goes back to the work of Göppert-Mayer<sup>18,19)</sup> (see the lecture by J.C. Gâcon in these proceedings). It is also possible to derive it, in an elegant way, from the method of the resolvent operator<sup>20)</sup>.

## 2.2. State vectors

The initial state  $i$  with symmetry  $\Gamma$  is characterized by the state vectors  $|i\Gamma\gamma\rangle$  where  $\gamma$  ( $\gamma = 1, 2, \dots, \dim \Gamma$ ) is a multiplicity label to be used if the dimension  $\dim \Gamma$  of the irreducible representation class (IRC)  $\Gamma$  of the group  $G$  is greater than 1. The state vector  $|i\Gamma\gamma\rangle$  is taken in the form

$$|i\Gamma\gamma\rangle \equiv |n\ell^N i\Gamma\gamma\rangle = \sum_{\alpha SLJa} |n\ell^N \alpha SLJa\Gamma\gamma\rangle c(\alpha SLJa\Gamma; i) \quad (4)$$

in terms of the  $O(3) \supset G$  symmetry adapted state vectors<sup>1,2)</sup>

$$|n\ell^N \alpha SLJa\Gamma\gamma\rangle = \sum_{M=-J}^J |n\ell^N \alpha SLJM\rangle (JM|Ja\Gamma\gamma) \quad (5)$$

The coefficients  $(JM|Ja\Gamma\gamma)$  in (5) are reduction coefficients to pass from the chain  $O(3) \supset O(2)$  characterizing the  $\{JM\}$  scheme to the chain  $O(3) \supset G$  characterizing the  $\{Ja\Gamma\gamma\}$  scheme ; they depend on the group  $G$  with a certain degree of freedom emphasized by the branching multiplicity label  $a$  to be used when  $\Gamma$  occurs several times in the IRC ( $J$ ) of  $O(3)$ . In contradistinction, the coefficients  $c(\alpha SLJa\Gamma; i)$  in (4) depend on the Hamiltonian employed for obtaining the initial state  $i$ . Similarly, for the final state  $f$  with symmetry  $\Gamma'$ , we have the state vectors

$$|f\Gamma'\gamma') \equiv |n\ell^N f\Gamma'\gamma') = \sum_{\alpha' S' L' J' a'} |n\ell^N \alpha' S' L' J' a' \Gamma' \gamma') c(\alpha' S' L' J' a' \Gamma'; f) \quad (6)$$

in terms of  $O(3) \supset G$  symmetry adapted state vectors. The only good quantum numbers for the initial and final state vectors are  $\Gamma\gamma$  and  $\Gamma'\gamma'$ , respectively. Although, the state vectors  $|i\Gamma\gamma)$  and  $|f\Gamma'\gamma')$  are developed in a weak-field basis, it is to be noted that the intensity calculation to be conducted in what follows is valid for any strength (weak, intermediate or strong) of the crystalline field.

### 2.3. Transition matrix element

By using a quasi-closure approximation, it can be shown that the transition matrix element  $M_{i \rightarrow f}$  between the state vectors  $|i\Gamma\gamma)$  and  $|f\Gamma'\gamma')$  is given by

$$M_{i \rightarrow f} \equiv M_{i(\Gamma\gamma) \rightarrow f(\Gamma'\gamma')} = (f\Gamma'\gamma' | H_{eff} | i\Gamma\gamma) \quad (7)$$

where  $H_{eff}$  is an effective operator<sup>7,8)</sup>. This operator may be written as<sup>12)</sup>

$$H_{eff} = \sum_{k=0,1,2} \sum_{k_S k_L} C[(k_S k_L) k] \left( \{\mathcal{E}_1 \mathcal{E}_2\}^{(k)} \cdot \mathbf{W}^{(k_S k_L) k} \right) \quad (8)$$

In equation (8),  $\mathbf{W}^{(k_S k_L) k}$  is an electronic double tensor of spin rank  $k_S$ , orbital rank  $k_L$  and total rank  $k$ . The information on the polarization of the two photons is contained in the tensor product  $\{\mathcal{E}_1 \mathcal{E}_2\}^{(k)}$  of rank  $k = 0, 1$  or  $2$ . The right-hand side of (8) is a development in terms of scalar products  $(\cdot)$  with expansion coefficients  $C[(k_S k_L) k]$ . These coefficients depend on the ground configuration  $n\ell^N$  and on the configurations  $n\ell^{N-1}n'\ell'$  and/or  $n'\ell'^{4\ell'+1}n\ell^{N+1}$ , with  $\ell + \ell'$  odd, from which the states  $v$  arise.

Only the contributions  $(k_S = 0, k_L = 1, k = 1)$  and  $(k_S = 0, k_L = 2, k = 2)$  correspond to the standard theory originally developed by Axe<sup>3)</sup>. The other contributions  $(k_S \neq 0, k_L, k)$ , which may include  $(k_S = 1, k_L = 1, k = 0)$  and  $(k_S = 1, k_L = 1, k = 2)$ , correspond either to mechanisms introduced by various authors<sup>7-11)</sup> or to phenomenological contributions<sup>12)</sup>. The contributions  $(k_S = 0, k_L = k, k)$  and  $(k_S \neq 0, k_L, k)$  are often referred to as second-order and third-order mechanisms, respectively. It is in principle possible to find an expression for the parameters  $C[(k_S k_L) k]$ . Among the various contributions  $(k_S \neq 0, k_L, k)$ , the contribution  $(k_S = 1, k_L = 1, k = 0)$  arises from the spin-orbit interaction within the configuration  $n\ell^{N-1}n'\ell'$  as was shown for lanthanide ions<sup>7,8)</sup>.

The transition matrix element (7) is easily calculated by means of Wigner-Racah calculus for the chain  $O(3) \supset G$ . As a result, we have<sup>12)</sup>

$$M_{i(\Gamma\gamma) \rightarrow f(\Gamma'\gamma')} = \sum_{\alpha' S' L' J' a'} \sum_{\alpha S L J a} c(\alpha' S' L' J' a' \Gamma'; f)^* c(\alpha S L J a \Gamma; i) \\ \sum_{k_S k_L k} (-)^{k_S + k_L - k} C[(k_S k_L) k] \left( n \ell^N \alpha S L J \| W^{(k_S k_L) k} \| n \ell^N \alpha' S' L' J' \right)^* \\ \sum_{a'' \Gamma'' \gamma''} f \left( \begin{matrix} J & J' & k \\ a \Gamma \gamma & a' \Gamma' \gamma' & a'' \Gamma'' \gamma'' \end{matrix} \right)^* \{ \mathcal{E}_1 \mathcal{E}_2 \}_{a'' \Gamma'' \gamma''}^{(k)} \quad (9)$$

where the  $f$  symbol denotes an  $O(3) \supset G$  symmetry adapted coupling coefficient defined by<sup>1,2)</sup>

$$f \left( \begin{matrix} J & J' & k \\ a \Gamma \gamma & a' \Gamma' \gamma' & a'' \Gamma'' \gamma'' \end{matrix} \right) = \sum_{MM'q} (-)^{J-M} \left( \begin{matrix} J & k & J' \\ -M & q & M' \end{matrix} \right) \\ (JM|Ja\Gamma\gamma)^* (J'M'|J'a'\Gamma'\gamma') (kq|ka''\Gamma''\gamma'')$$

Equation (9) follows by developing (7) with the help of (4), (6) and (8).

#### 2.4. Intensity formula

The quantity of interest for a comparison between theory and experiment is the intensity  $S_{i(\Gamma) \rightarrow f(\Gamma')}$  of the two-photon transition between the initial state  $i$  and the final state  $f$ . This intensity is given by

$$S_{\Gamma \rightarrow \Gamma'} \equiv S_{i(\Gamma) \rightarrow f(\Gamma')} = \sum_{\gamma \gamma'} |M_{i(\Gamma\gamma) \rightarrow f(\Gamma'\gamma')}|^2 \quad (10)$$

By introducing (9) into (10) and using the factorization property<sup>1)</sup> for the  $f$  coefficients as well as the orthonormality-completeness property<sup>1)</sup> for the Clebsch-Gordan coefficients of the group  $G$ , we obtain the compact expression

$$S_{\Gamma \rightarrow \Gamma'} = \sum_{k, \ell} \sum_{r, s} \sum_{\Gamma''} I[k \ell r s \Gamma''; \Gamma \Gamma'] \sum_{\gamma''} \{ \mathcal{E}_1 \mathcal{E}_2 \}_{r \Gamma'' \gamma''}^{(k)} \left( \{ \mathcal{E}_1 \mathcal{E}_2 \}_{s \Gamma'' \gamma''}^{(\ell)} \right)^* \quad (11)$$

In equation (11), the parameter  $I$  reads

$$I[k \ell r s \Gamma''; \Gamma \Gamma'] = [\Gamma'']^{-1} [\Gamma] \sum_{J' a'} \sum_{J a} \sum_{\bar{J}' \bar{a}'} \sum_{\bar{J} \bar{a}} Y_k(J' a' \Gamma', J a \Gamma) \\ Y_\ell(\bar{J}' \bar{a}' \Gamma', \bar{J} \bar{a} \Gamma)^* \sum_{\beta} (J' a' \Gamma' + k r \Gamma'' | J a \beta \Gamma) (\bar{J}' \bar{a}' \Gamma' + \ell s \Gamma'' | \bar{J} \bar{a} \beta \Gamma)^* \quad (12)$$

where  $Y_k$  is defined by

$$Y_k(J' a' \Gamma', J a \Gamma) = [J]^{-1/2} \sum_{\alpha' S' L'} \sum_{\alpha S L} \sum_{k_S k_L} c(\alpha' S' L' J' a' \Gamma'; f)^* c(\alpha S L J a \Gamma; i) \\ C[(k_S k_L) k] (-)^{k_S + k_L - k} (n \ell^N \alpha S L J \| W^{(k_S k_L) k} \| n \ell^N \alpha' S' L' J')^* \quad (13)$$

and  $Y_\ell$  by a relation similar to (13). In (12) the ( + | ) coefficients stand for isoscalar factors of the chain  $O(3) \supset G$  and the labels  $\beta$  are internal multiplicity labels to be used for those Kronecker products which are not multiplicity-free<sup>1)</sup>.

## 2.5. Properties and rules

The  $I$  parameters in (11) can be calculated in an *ab initio* way or can be considered as phenomenological parameters. In both approaches, the following properties and rules are of central importance.

Property 1. In the general case, we have the (hermitean) property

$$I[\ellksr\Gamma''; \Gamma\Gamma']^* = I[k\lrs\Gamma''; \Gamma\Gamma'] \quad (14)$$

which ensures that  $S_{\Gamma \rightarrow \Gamma'}$  is a real quantity.

Property 2. In the case where the group  $G$  is multiplicity-free, we have the factorization formula

$$I[k\lrs\Gamma''; \Gamma\Gamma'] = \chi[kr\Gamma''; \Gamma\Gamma'] \chi[\ell s\Gamma''; \Gamma\Gamma']^* \quad (15)$$

where the function  $\chi$  is defined through

$$\chi[kr\Gamma''; \Gamma\Gamma'] = [\Gamma'']^{-1/2} [\Gamma]^{1/2} \sum_{J'a'} \sum_{Ja} Y_k(J'a'\Gamma', Ja\Gamma) (J'a'\Gamma' + kr\Gamma''|Ja\Gamma)$$

(In a less restrictive sense, equation (15) is valid when the Kronecker product  $\Gamma'^* \otimes \Gamma$ , of the complex conjugate IRC of  $\Gamma'$  by the IRC  $\Gamma$ , is multiplicity-free.)

The number of independent parameters  $I$  in the expansion (11) can be *a priori* determined from the two following selection rules used in conjunction with Properties 1 and 2.

Rule 1. In order to have  $S_{\Gamma \rightarrow \Gamma'} \neq 0$ , it is necessary that

$$\Gamma'' \subset \Gamma'^* \otimes \Gamma \quad \Gamma'' \subset (k_g) \quad \Gamma'' \subset (\ell_g) \quad (16)$$

where  $(k_g)$  and  $(\ell_g)$  are *gerade* IRC's of the group  $O(3)$  associated to the integers  $k$  and  $\ell$ , respectively.

Rule 2. The sum over  $k$  and  $\ell$  in the intensity formula (11) is partially controlled by the selection rule

$$\mathcal{E}_1 \neq \mathcal{E}_2 : k, \ell = 1, 2 \text{ for 2nd-order} \quad \text{or} \quad k, \ell = 0, 1, 2 \text{ for 2nd-order + 3rd-order}$$

or

$$\mathcal{E}_1 = \mathcal{E}_2 : k, \ell = 2 \text{ for 2nd-order} \quad \text{or} \quad k, \ell = 0, 2 \text{ for 2nd-order + 3rd-order}$$

according to as the two photons have different or the same polarization. (Note that the situation  $\mathcal{E}_1 = \mathcal{E}_2$  surely occurs for identical photons but may also occur for non-identical photons.)

## 2.6. Discussion

For most of the cases of interest, there is no summation on  $r$  and  $s$ , two branching multiplicity labels of type  $a$ , in the intensity formula (11). (In other words, the frequency of  $\Gamma''$  in  $(k_g)$  and  $(\ell_g)$  is rarely greater than 1.) The group-theoretical selection rules (16) impose strong limitations on the summation over  $\Gamma''$  in (11) once  $\Gamma$  and  $\Gamma'$  are fixed and the range of values of  $k$  and  $\ell$  is chosen.

The number of independent intensity parameters  $I$  in the formula (11) depends on : (i) the nature of the photons, cf. Rule 2 ; (ii) the group  $G$ , cf. Rule 1 ; (iii) the conjugation property (14), cf. Property 1 ; (iv) the use of  $k_S = 0$  (second-order mechanisms) or  $k_S = 0$  and  $k_S \neq 0$  (second- plus third-order mechanisms), cf. Rule 2 ; (v) the (weak-, intermediate- or strong-field) state vectors used in conjunction with equations (12) and (13).

Points (i)-(iii) depend on external physical conditions. On the other hand, points (iv) and (v) are model-dependent. In particular, in the case where the  $J$ -mixing, cf. point (v), can be neglected, a situation often of interest for lanthanide ions, the summations on  $k$  and  $\ell$  in (11) are further reduced by the triangular rule  $|J - J'| \leq k, \ell \leq J + J'$ , where  $J$  and  $J'$  are the total angular quantum numbers for the initial and final states, respectively. Similar restrictions apply to  $k_S$  and  $k_L$  in (13) if the  $S$ - and  $L$ -mixing are neglected.

The computation, via equations (12) and (13), of the  $I$  parameters generally is a difficult task. Therefore, they may be considered, at least in a first step, as phenomenological parameters. In this respect, equations (12) and (13) should serve as a guide for reducing the number of  $I$  parameters.

Once the number of independent parameters  $I$  in the formula (11) has been determined, we can obtain the polarization dependence of the intensity strength  $S_{\Gamma \rightarrow \Gamma'}$  by calculating the tensor products  $\{\mathcal{E}_1 \mathcal{E}_2\}_{a'' \Gamma'' \gamma''}^{(K)}$  (with  $K = k, \ell$  and  $a'' = r, s$ ) occurring in (11). For this purpose, we use the development

$$\{\mathcal{E}_1 \mathcal{E}_2\}_{a'' \Gamma'' \gamma''}^{(K)} = \sum_{Q=-K}^K \{\mathcal{E}_1 \mathcal{E}_2\}_Q^{(K)} (KQ|Ka''\Gamma''\gamma'') \quad (17)$$

in terms of the spherical components  $\{\mathcal{E}_1 \mathcal{E}_2\}_Q^{(K)}$ , the coefficients in (17) being reduction coefficients for the chain  $O(3) \supset G$ . Then, we use in turn the development

$$\{\mathcal{E}_1 \mathcal{E}_2\}_Q^{(K)} = (-)^{K-Q} [K]^{1/2} \sum_{m=-1}^1 \sum_{m'=-1}^1 \begin{pmatrix} 1 & K & 1 \\ m & -Q & m' \end{pmatrix} (\mathcal{E}_1)_m (\mathcal{E}_2)_{m'}$$

in terms of the spherical components  $(\mathcal{E}_\lambda)_q$  defined by (2) or (3) for circular or linear polarization, respectively.

## 2.7. Illustration

As a pedagogical example, let us consider the case of the two-photon absorption (intra-configurational) transition  $^7F_0 \rightarrow ^5D_0$  for the configuration  $4f^6$  in tetragonal symmetry (with  $G \equiv C_{4v}$  or  $D_{2d}$ ). In this case, we have  $\Gamma = A_1$  for the

initial state and  $\Gamma' = A_1$  for the final state, whatever the strength of the crystalline field is. Rule 1 then yields  $\Gamma'' = A_1$  and, consequently, there is no sum on the label  $\gamma''$  in (11). Furthermore, there is no sum on the branching multiplicity labels  $r$  and  $s$  in the intensity formula (11). Let us consider an experimental situation where the two photons are identical (one-color beam arrangement) so that  $\mathcal{E}_1 \equiv \mathcal{E}_2 = \mathcal{E}$ . We continue with a model characterized (in addition to the symmetry  $C_{4v}$  or  $D_{2d}$ ) by the use of second- plus third-order mechanisms. Thus, according to Rule 2, the indices  $k, \ell$  in (11) may assume the values 0 and 2. By introducing the abbreviation  $I(k\ell) \equiv I[k\ell rs\Gamma'' = A_1; \Gamma = A_1, \Gamma' = A_1]$ , we are left with 3 *a priori* independent parameters (cf. Property 1), viz.,  $I(00)$ ,  $I(02) = I(20)^*$  and  $I(22)$ . Taking the wave-vector  $\vec{k}$  of the two photons parallel to the crystallographic  $c$ -axis, we have

$$\{\mathcal{E}\mathcal{E}\}_{A_1}^0 \equiv \{\mathcal{E}\mathcal{E}\}_0^0 = \frac{-1}{\sqrt{3}} \text{ or } 0 \quad \text{and} \quad \{\mathcal{E}\mathcal{E}\}_{A_1}^2 \equiv \{\mathcal{E}\mathcal{E}\}_0^2 = \frac{3\cos^2\theta - 1}{\sqrt{6}} \text{ or } 0 \quad (18)$$

for linear or circular polarization, respectively. Finally, the intensity strength  $S_{A_1 \rightarrow A_1}$  is easily obtained by introducing (18) into (11). This leads to

$$S_{A_1 \rightarrow A_1} = r^2 + s(3\cos^2\theta - 1) + t^2(3\cos^2\theta - 1)^2 \quad \text{or} \quad 0 \quad (19)$$

according to whether as the polarization is linear or circular, respectively. Here, the real parameter  $s$  and the two non-negative parameters  $r^2$  and  $t^2$  are defined by

$$r^2 = \frac{I(00)}{3} \quad s = \frac{-I(02) - I(02)^*}{3\sqrt{2}} \quad t^2 = \frac{I(22)}{6}$$

In the intensity formula (19), the two first terms (in  $r^2$  and  $s$ ) arise from third-order mechanisms while the third one (in  $t^2$ ) comes from second-order mechanisms. Only the scalar term (in  $r^2$ ) contributes to  $S_{A_1 \rightarrow A_1}$  in the absence of  $J$ -mixing.

Equation (19) has been applied<sup>13)</sup> to the cases of  $\text{Sm}^{2+}:\text{BaClF}$ ,  $\text{Sm}^{2+}:\text{SrClF}$  and  $\text{Eu}^{3+}:\text{LuPO}_4$ . Neither the conventional second-order term (in  $t^2$ ) nor the scalar third-order term (in  $r^2$ ) are sufficient to reproduce the experimental data. Indeed, on the basis of fitting procedures<sup>13)</sup>, a good agreement between theory and experiment requires in these cases that the three terms (in  $r^2$ ,  $t$ , and  $s^2$ ) contribute to the intensity strength (19). As a conclusion, the model inherent to equation (19), the ingredients of this model being : (symmetry, second- plus third-order mechanisms,  $J$ -mixing), is appropriate to the  $^7F_0 \rightarrow ^5D_0$  two-photon transition for  $\text{Sm}^{2+}:\text{BaClF}$ ,  $\text{Sm}^{2+}:\text{SrClF}$  and  $\text{Eu}^{3+}:\text{LuPO}_4$ .

Similar models have been applied to the two-photon transitions<sup>13)</sup>  $^7F_0(\Gamma = A_1) \rightarrow ^5D_2(\Gamma' = A_1, B_1, B_2, E)$  for the tetragonal compound  $\text{Sm}^{2+}:\text{BaClF}$  and to the two-photon transitions<sup>17)</sup>  $^3A_2(\Gamma = T_2) \rightarrow ^3T_2(\Gamma' = A_2, E, T_1, T_2)$  for the cubical compound  $\text{Ni}^{2+}:\text{MgO}$ . In both cases, we have found that second-order mechanisms are sufficient to describe the transitions. More precisely, the model : (symmetry, second-order mechanisms,  $S$ - and  $L$ -mixing but no  $J$ -mixing) works

for  $\text{Sm}^{2+}:\text{BaClF}$  while the model : (symmetry, second-order mechanisms,  $S$ -,  $L$ - and  $J$ -mixing) works for  $\text{Ni}^{2+}:\text{MgO}$ .

### 3. INTER-CONFIGURATIONAL TWO-PHOTON TRANSITIONS

#### 3.1. Sketch of the theory

We now consider two-photon transitions between Stark levels arising from the configurations  $n\ell^N$  and  $n\ell^{N-1}n'\ell'$  of opposite parities ( $\ell + \ell'$  odd). For the sake of simplicity, we deal here with identical photons. The initial (i.e.,  $|i\Gamma\gamma\rangle$ ) and final (i.e.,  $|f\Gamma'\gamma'\rangle$ ) state vectors are taken in the form

$$\begin{aligned} |n\ell^N i\Gamma\gamma\rangle &= \sum_{\alpha SLJa} |n\ell^N \alpha SLJa\Gamma\gamma\rangle c(\alpha SLJa\Gamma; i) \\ |n\ell^{N-1}n'\ell' f\Gamma'\gamma'\rangle &= \sum_{\alpha' S'L'J'a'} |n\ell^{N-1}n'\ell' \alpha' S'L'J'a'\Gamma'\gamma'\rangle c(\alpha' S'L'J'a'\Gamma'; f) \end{aligned} \quad (20)$$

to be compared with equations (4) and (6).

It is clear that the transition matrix element

$$M_{i(\Gamma\gamma) \rightarrow f(\Gamma'\gamma')} = \sum_v \frac{1}{\Delta} \left( f\Gamma'\gamma' | \vec{D} \cdot \vec{\mathcal{E}} | v\Gamma_v \gamma_v \right) \left( v\Gamma_v \gamma_v | \vec{D} \cdot \vec{\mathcal{E}} | i\Gamma\gamma \right)$$

is identically zero. In order to obtain  $M_{i(\Gamma\gamma) \rightarrow f(\Gamma'\gamma')} \neq 0$ , it is necessary to pollute (20), as well as the intermediate state vectors, with state vectors of the type  $|n\ell^{N-1}n'\ell' x'\Gamma'\gamma'\rangle$  and  $|n\ell^N x\Gamma\gamma\rangle$ , respectively. This may be achieved by using first-order time-independent perturbation theory where the polluting agent is the crystal-field potential  $H_3$  of odd order, which is static or dynamic according to as the group  $G$  does not or does have a center of inversion. Hence, we produce state vectors noted  $|n\ell^N i\Gamma\gamma\rangle$  and  $|n\ell^{N-1}n'\ell' f\Gamma'\gamma'\rangle$  from which we can calculate, in a 2nd-order time-dependent plus 1st-order time-independent scheme, a non-vanishing transition matrix element

$$M_{i(\Gamma\gamma) \rightarrow f(\Gamma'\gamma')} = \sum_v \frac{1}{\Delta} \langle f\Gamma'\gamma' | \vec{D} \cdot \vec{\mathcal{E}} | v\Gamma_v \gamma_v \rangle \langle v\Gamma_v \gamma_v | \vec{D} \cdot \vec{\mathcal{E}} | i\Gamma\gamma \rangle$$

Then, we apply a quasi-closure approximation both for the initial, intermediate, and final state vectors and the transition matrix element. This approximation can be summarized by  $E(n'\ell') - E(n\ell) = 2\hbar\omega$ . We thus obtain a closed form formula for  $M_{i(\Gamma\gamma) \rightarrow f(\Gamma'\gamma')}$  (see Ref. [20]).

At this stage, it should be mentioned that the so-obtained formula is equivalent to that we would obtain, within the just mentioned approximation, by using third-order mechanisms described by

$$\begin{aligned} M_{i(\Gamma\gamma) \rightarrow f(\Gamma'\gamma')} &= \sum_{v_1 v_2} \frac{1}{\Delta(v_1)} \frac{1}{\Delta(v_2)} (f\Gamma'\gamma' | \vec{D} \cdot \vec{\mathcal{E}} | v_1 \Gamma_1 \gamma_1) (v_1 \Gamma_1 \gamma_1 | \vec{D} \cdot \vec{\mathcal{E}} | v_2 \Gamma_2 \gamma_2) \times \\ &\quad \times (v_2 \Gamma_2 \gamma_2 | H_3 | i\Gamma\gamma) + \text{term } [\vec{D} \cdot \vec{\mathcal{E}} | H_3 | \vec{D} \cdot \vec{\mathcal{E}}] + \text{term } [H_3 | \vec{D} \cdot \vec{\mathcal{E}} | \vec{D} \cdot \vec{\mathcal{E}}] \end{aligned}$$

where the initial, intermediate and final state vectors are non-polluted.

By following the same line of reasoning as in the case of intra-configurational transitions, we are left with the intensity formula<sup>20)</sup>

$$S_{\Gamma \rightarrow \Gamma'} = \text{Re} \left[ \sum_{k,\ell=0,2} \sum_{r,s} \sum_{\Gamma''} I_1[k\ell rs\Gamma''; \Gamma\Gamma'] \sum_{\gamma''} \{\mathcal{E} \mathcal{E}\}_{r\Gamma''\gamma''}^{(k)} \left( \{\mathcal{E} \mathcal{E}\}_{s\Gamma''\gamma''}^{(\ell)} \right)^* \right. \\ \left. + \sum_{k=0,2} \sum_{r,s} \sum_{\Gamma''} I_2[k2rs\Gamma''; \Gamma\Gamma'] \sum_{\gamma''} \{\mathcal{E} \mathcal{E}\}_{r\Gamma''\gamma''}^{(k)} \{\mathcal{E} \mathcal{E}\}_{s\Gamma''\gamma''}^{(2)} \right] \quad (21)$$

which parallels the formula (11). A detailed expression of the intensity parameters  $I_1$  and  $I_2$  will be found in the thesis by Daoud<sup>20)</sup> and in forthcoming papers.

### 3.2. Illustration

Let us consider the case of the configuration  $4f$  in tetragonal symmetry with  $G \equiv C_{4v}$  and examine the two-photon transitions between the Stark levels of the shells  $4f$  and  $5d$  (i.e.,  $n\ell \equiv 4f$ ,  $N \equiv 1$ ,  $n'\ell' \equiv 5d$ ). There are four possible transitions since the initial and final states may have the symmetries  $\Gamma_6$  and  $\Gamma_7$ . For a linear polarization, the application of the intensity formula (21) leads to

$$S_{\Gamma_6 \rightarrow \Gamma_7} = f\pi_2 + g\pi_3 + h\pi_4 + i\pi_5, \quad S_{\Gamma_7 \rightarrow \Gamma_7} = a' + b'\pi_1 + c'\pi_1^2 + d'\pi_2 + e'\pi_3 \\ S_{\Gamma_7 \rightarrow \Gamma_6} = f'\pi_2 + g'\pi_3 + h'\pi_4 + i'\pi_5, \quad S_{\Gamma_6 \rightarrow \Gamma_6} = a + b\pi_1 + c\pi_1^2 + d\pi_2 + e\pi_3$$

where the angular functions  $\pi_i$  ( $i = 1, 2, 3, 4, 5$ ) are defined by

$$\pi_1 = 3\cos^2\theta - 1, \quad \pi_2 = \sin^2 2\theta, \quad \pi_3 = \pi_2 \cos 2\varphi, \quad \pi_4 = \sin^4 \theta \cos^2 2\varphi, \quad \pi_5 = \sin^4 \theta - \pi_4$$

The various parameters  $a, \dots, i$  and  $a', \dots, i'$  are simple functions<sup>20)</sup> of the intensity parameters  $I_1$  and  $I_2$  occurring in (21).

### 4. CLOSING REMARKS

We have shown how  $O(3) \supset G$  symmetry adaptation allows to derive intensity formulas for intra- and inter-configurational two-photon transitions for ions in molecular or solid-state environments. In particular, the number of independent parameters required for describing the polarization dependence of the transitions is determined by an ensemble of properties and rules which combine symmetry and physical considerations. The main results of this paper are formulas (11) and (21) for intra- and inter-configurational transitions, respectively.

The polarization factors in (11) and (21) are under the control of the experimentalist. Both formulas depend on expansion coefficients  $c(\alpha SLJa\Gamma; i)$  and  $c(\alpha' S'L'J'a'\Gamma'; f)$ . These coefficients (model dependent) can be obtained by optimizing Hamiltonians, for the ion in its environment, involving at least Coulomb, spin-orbit and crystal-field interactions ; the introduction of more sophisticated interactions may be useful to take covalency effects into account<sup>2)</sup>. Alternatively, the expansion coefficients can be considered as free parameters. Furthermore, in (11) and (21) we have reduced matrix elements (configuration dependent), isoscalar factors for  $O(3) \supset G$  (group theory dependent), and  $C[(k_S k_L)k]$  parameters (mechanisms dependent). As a conclusion, there are three ways to deal with the intensity

parameters in (11) and (21) : they can be calculated from first principles, or considered as phenomenological parameters or determined in a mixed approach.

The author is very grateful to the Organizing Committee of the School for inviting him to give this lecture.

#### REFERENCES

- 1 Kibler, M., C. R. Acad. Sc. (Paris) B 268, 1221 (1969) ; Kibler, M.R. and Guichon, P.A.M., Int. J. Quantum Chem. 10, 87 (1976) ; Kibler, M.R. and Grenet, G., Int. J. Quantum Chem. 11, 359 (1977) ; Kibler, M.R., in : Recent Advances in Group Theory and Their Application to Spectroscopy, Ed. J.C. Donini (Plenum, 1979) ; Int. J. Quantum Chem. 23, 115 (1983) ; Croat. Chem. Acta 57, 1075 (1984).
- 2 Kibler, M. and Grenet, G., Report LYCEN 8656 (IPN Lyon, 1986).
- 3 Axe, J.D., Jr., Phys. Rev. 136, A42 (1964).
- 4 Inoue, M. and Toyozawa, Y., J. Phys. Soc. Japan 20, 363 (1965).
- 5 Bader, T.R. and Gold, A., Phys. Rev. 171, 997 (1968).
- 6 Apanasevich, P.A., Gintoft, R.I., Korolkov, V.S., Makhanek, A.G. and Skripko, G.A., Phys. Status Solidi (b) 58, 745 (1973) ; Makhanek, A.G. and Skripko, G.A., Phys. Status Solidi (a) 53, 243 (1979) ; Yuguryan, L.A., Preprints N° 232 and 233, Inst. Fiz. Akad. Nauk BSSR, Minsk (1980) ; Makhanek, A.G., Korolkov, V.S. and Yuguryan, L.A., Phys. Status Solidi (b) 149, 231 (1988).
- 7 Judd, B.R. and Pooler, D.R., J. Phys. C 15, 591 (1982).
- 8 Downer, M.C. and Bivas, A., Phys. Rev. B 28, 3677 (1983) ; Downer, M.C., in : Laser Spectroscopy of Solids II, Ed. W.M. Yen (Springer, 1989).
- 9 Reid, M.F. and Richardson, F.S., Phys. Rev. B 29, 2830 (1984).
- 10 Sztucki, J. and Strek, W., Phys. Rev. B 34, 3120 (1986) ; Chem. Phys. Lett. 125, 520 (1986) ; Chem. Phys. 143, 347 (1990).
- 11 Jankowski, K. and Smentek-Mielczarek, L., Molec. Phys. 60, 1211 (1987) ; Smentek-Mielczarek, L. and Hess, B.A., Jr., Phys. Rev. B 36, 1811 (1987).
- 12 Kibler, M. and Gâcon, J.C., Croat. Chem. Acta 62, 783 (1989).
- 13 Gâcon, J.C., Marcerou, J.F., Bouazaoui, M., Jacquier, B. and Kibler, M., Phys. Rev. B 40, 2070 (1989) ; Gâcon, J.C., Jacquier, B., Marcerou, J.F., Bouazaoui, M. and Kibler, M., J. Lumin. 45, 162 (1990) ; Gâcon, J.C., Bouazaoui, M., Jacquier, B., Kibler, M., Boatner, L.A. and Abraham, M.M., Eur. J. Solid State Inorg. Chem. 28, 113 (1991).
- 14 Kibler, M., in : Symmetry and Structural Properties of Condensed Matter, Eds. W. Florek, T. Lulek and M. Mucha (World, 1991).
- 15 Campochiaro, C., McClure, D.S., Rabinowitz, P. and Dougal, S., Phys. Rev. B 43, 14 (1991).
- 16 Kibler, M. and Daoud, M., Report LYCEN 9117 (IPN Lyon, 1991).
- 17 Sztucki, J., Daoud, M. and Kibler, M., Phys. Rev. B (in press).
- 18 Loudon, R., The Quantum Theory of Light (Clarendon, 1973).
- 19 Cohen-Tannoudji, C., Dupont-Roc, J. and Grynberg, G., Processus d'interaction entre photons et atomes (InterEditions et Editions du CNRS, 1988).
- 20 Daoud, M., thèse de Doctorat (Université Lyon-1, in preparation).